



Photocatalytic removal of methylmercury assisted by UV-A irradiation

Cristian Miranda^a, Jorge Yáñez^a, David Contreras^a, Rafael Garcia^a, Wilson F. Jardim^b, Héctor D. Mansilla^{a,*}

^aFacultad de Ciencias Químicas, Universidad de Concepción, Casilla 160-C, Concepción, Chile

^bInstituto de Química, Universidade Estadual de Campinas, CP 6154, 130871-970 Campinas, São Paulo, Brazil

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ABSTRACT

The present study evaluates the removal of methylmercury from aqueous solutions by TiO₂ photocatalysis using UV-A irradiation. To assess the weight of the variables pH and amount of catalyst, a factorial design was used when planning the experiments. Methylmercury was determined by the difference between total mercury and inorganic mercury. The optimal conditions for methylmercury removal are low amounts of catalyst and an alkaline pH. Under optimal conditions, more than 95% of methylmercury removal was achieved after 2 min irradiation. Methylmercury can be removed in the presence of nitrogen or oxygen under different mechanism pathways. In the presence of nitrogen, the reaction proceed by forming water soluble compounds, such as methanol or more oxidised moieties. In the presence of oxygen, the reaction slows due to competition between oxygen and Hg (II) for conduction band electrons. In saturated oxygen solutions, the main reaction products were CH₄, CO and CO₂. To recover the reduced mercury released from the reactor, copper powder was arranged in a trapping device amalgamating Hg⁰, achieving above 90% of retention yield.

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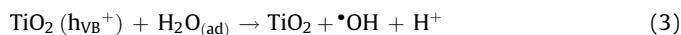
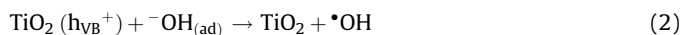
1. Introduction

Methylmercury (CH₃Hg⁺) is a neurotoxic compound and this form of mercury is the most easily bioaccumulated in living organisms, causing irreversible damage to the central nervous system [1]. In the environment, methylmercury is formed primarily by a biomethylation process, which consists in the transformation of divalent inorganic mercury (Hg²⁺) into CH₃Hg⁺ by sulphate-reducing bacteria present in anoxic environments, such as estuarine and lake-bottom sediments. Mercury enters the environment from a large number of miscellaneous sources related to human activities, including fluorescent bulbs, unsafe disposal of laboratory chemicals, batteries, broken thermometers, amalgam tooth fillings, fungicides, pharmaceutical products, reaching sediments where it accumulates, in special close to old chloro-alkali factories [2–4].

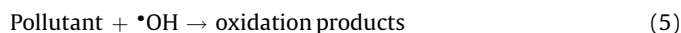
Methylmercury is the most common species of organic mercury. In contrast, phenylmercury and dimethylmercury, which are other examples of organic mercury used for medical and commercial purposes, are rarely found in the environment. Methylmercury and ethylmercury compounds were once used as fungicides; however, their use was banned in the 1970s due to their adverse health effects.

The most commonly used alternatives to remove Hg²⁺ from the environment are sorption, ion exchange, precipitation and electrochemical techniques. In general, these techniques are inefficient and generate secondary wastes that must often be disposed as hazardous materials. In recent years, photocatalysis has been proposed as a new promising alternative to reduce Hg²⁺ to Hg⁰ from Hg (II) salts [5–8] or phenylmercury [9].

In recent years, photocatalysis has gained considerable attention due to its ability to degrade a wide class of pollutants [10–12]. When aqueous TiO₂ suspension is irradiated with photons energy is greater than its band gap (E_g , 3.2 eV), it is well established that the initial step involves the generation of a charge carrier pair (e^-/h^+) resulting in the formation of strong oxidants, such as hydroxyl radical and superoxide radical anion (Eqs. (1–4)):

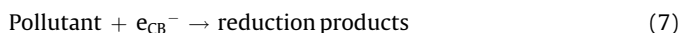
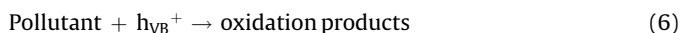


Pollutant can be destroyed by radicals attack, direct hole oxidation, or reduction via conduction band electrons (Eqs. (5–7)):



* Corresponding author. Tel.: +56 41 2204600; fax: +56 41 2245974.

E-mail address: hmansill@udec.cl (H.D. Mansilla).



In the photocatalytic reduction of inorganic species, an electron donor is needed to facilitate the electron supply to the catalyst's valence band. By photons absorption these electrons are promoted to the conduction band, where the reduction process takes place [8]. In the case of an organometallic compound, such as methylmercury, the electron donor (methyl group) and electron-acceptor (Hg^{2+}) are concurrently present in the same molecule, suggesting that it is possible to avoid the external addition of a sacrificial electron donor.

The aim of the present work is to reduce Hg (II) in methylmercury to Hg^0 by TiO_2 heterogeneous photocatalysis assisted by UV-A irradiation, simultaneously oxidising the organic matter (methyl group).

The reaction conditions were optimised by simultaneously modifying the pH and the amount of titania. Also, the fate of organic matter during the photocatalytic process was determined. Finally, the released Hg^0 was trapped using Cu^0 pellets to amalgamate the metal vapour.

2. Experimental

2.1. Materials

Methylmercury chloride (CH_3HgCl , minimum 95% purity) was purchased from Pfaltz & Bauer Inc. (USA) and HgCl_2 (>99.5%) was obtained from Merck (Germany). Titanium dioxide P-25 was obtained from Degussa (Germany). Potassium permanganate (>95%), hydroxylamine chloride and tin chloride, low in mercury (max. 5×10^{-6} %Hg), analytical grade were obtained from Merck and used without further purification. Reagents such as acids and bases were analytical grade (Merck). Highly pure gases (N_2 , O_2) and Fisher–Tropsch gas mixture were purchased from AGA (Chile).

2.2. Irradiation procedure

The photochemical reactor consisted of a 350-ml borosilicate flask illuminated by a commercial Solarium Philip HB311 arranged with 6×20 W lamps ($\lambda = 300\text{--}400$ nm, with a photonic flux of 540 W m^{-2} at 360 nm determined with a UVP radiometer, model UVX). The catalyst was used in suspension at pH ranging from 4 to 11 and amounts of TiO_2 ranging from 0.06 g L^{-1} and 0.8 g L^{-1} . The MeHg (100 mL, $100 \mu\text{g L}^{-1}$ in Hg basis) solution was always maintained under magnetic stirring and nitrogen bubbling (100 mL min^{-1}). The presence of nitrogen follows two objectives: (1) keep the reaction system in absence of oxygen and (2) serve as carrier gas to purge the reduced mercury (Hg^0) out of the reactor at the same time it is formed. The reduced mercury carried in the nitrogen stream was bubbled and trapped in a permanganate solution (10%, w/v).

2.3. Mercury determination by AAS

In the course of the reaction liquid samples were taken from the photocatalytic reactor and filtered using a nitrocellulose Millipore membrane (2.5 cm, $0.2 \mu\text{m}$). Samples (10 mL) were digested with 5 mL of *aqua regia* (3.75 mL HCl + 1.25 mL HNO_3) and 25 mL of 5% KMnO_4 solution during 1 h. Temperature was maintained at 95°C in a thermostat bath. After digestion, 15 mL of 5% (w/v) hydroxylamine chloride were added in order to eliminate the excess of KMnO_4 . Digested samples were diluted with nanopure water until 100 mL in volumetric flasks.

Total mercury was determined using the technique of Hg^0 cold vapour generation with Sn (II) using an Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 100) coupled to a flow injection analyser (Perkin Elmer FIAS 100) [13]. The instrument was operated at 253.7 and 0.7 nm slit. With a sample volume of 1 mL, the detection limit was $0.3 \mu\text{g L}^{-1}$ in a calibration range between 0.3 and $50 \mu\text{g L}^{-1}$ and a precision of $\pm 0.4 \mu\text{g L}^{-1}$ for a $10.3 \mu\text{g L}^{-1}$ solution. The total amount of Hg^0 formed during the course of the reaction was determined by the difference between the initial Hg concentration in the reactor and the amount of remaining Hg determined in solution during the reaction.

A second procedure used to determine Hg^0 coming from the reaction system was to directly connect the outlet gases to the AA spectrometer. This experiment allows the on-line determination of gaseous Hg^0 . A standard solution of HgCl_2 ($100 \mu\text{g L}^{-1}$, Hg basis) was reduced in the reactor using SnCl_2 in order to generate Hg^0 vapour.

2.4. Chromatographic analysis of gases in the course of the reaction

To evaluate the fate of the methyl group during the photocatalytic reaction under reductive conditions (N_2 flow), the reaction was carried out under the same conditions already described (item 2.2). In this case, the initial concentration of methylmercury was 100 mg L^{-1} (Hg basis). The gas stream outlet was connected to a gas chromatograph equipped with a thermal conductivity detector (Aerograph A-90P). A stainless steel packed column (Supelco Custom Column 0618-2007, $10 \text{ ft} \times 1/8 \text{ in.}$) filled with support 60180 carbosieve SII (Supelco) was maintained at 110°C . Helium was used as carrier gas at 100 mL min^{-1} . To trap Hg^0 before reaching the column, a trap with metallic Cu^0 was installed before the GC sample inlet. The gaseous products formed during 2 min of reaction were purged with nitrogen into an injection valve (1 mL loop) before the gas was introduced into the GC. As standard, 1 mL of Fischer–Tropsch (F–T) gas mixture was injected into the chromatograph. The composition of the F–T gas was: 32% CO , 32% H_2 , 12% CO_2 , 18% CH_4 and 6% N_2 .

2.5. Chromatographic determination of methanol in the solution after the reaction

The evolution of water soluble compounds during the photocatalytic reaction of methylmercury (100 mg/L) under optimised conditions was followed by GC/MS analysis. Samples were collected directly from the aqueous phase after 2 min of reaction. Determinations were carried out in a gas chromatograph (Agilent 7890) equipped with a Turbomatrix 40 trap headspace (PerkinElmer) a Mass Filter (Agilent 5975C) and a DB624 column ($30 \text{ m}/0.32 \text{ mm}/1.8 \mu\text{m}$). The oven temperature program was: 40°C (5 min), 15°C/min , 100°C (2 min). Methanol was identified by mass spectra and by comparison with a standard (retention time 3.4 min).

2.6. Optimisation by response surface modelling

A response surface modelling of the photocatalytic reaction was performed based on a central composite circumscribed design, composed by a factorial model, star points and three replicated central points. The methodology has been described for industrial effluents, dyes and pharmaceuticals [14–17]. In a first approach, the variables pH (ranging from 4 to 10) and amount of catalyst (ranging from 0.2 to 0.8 g L^{-1}) were evaluated by a 2^n model. For n variables and two levels (low and high, or -1 and $+1$) the total number of experiments is determined by the expression: $2^n + 2n + 3$. After perform the 11 experiments ($n = 2$), the main conclusion was that the optimal conditions to remove CH_3Hg^+ are

found at alkaline pH and very low amount of catalyst (below 0.2 g L^{-1}). The reaction was stopped after 2 min irradiation. In a second approach, both variables were restricted to a narrow ranges: pH (9–11) and TiO_2 amount (0.06 – 0.2 g L^{-1}). Only the last model is analysed in the present work.

The software MODDE 7 was used in order to carry out the calculations and evaluate the results, building the polynomial and the surface response 3D representation.

2.7. Trapping of Hg^0 in amalgam with copper pellets

The volatile Hg^0 produced in the reaction system was trapped in a glass column packed with 0.5 g of finely divided copper pellets (Merck, particle size $<63 \mu\text{m}$). Three forms of copper were assayed: chips, thin foils ($0.5 \text{ cm} \times 0.5 \text{ cm}$) and fine powder ($<63 \mu\text{m}$). In order to quantify the amount of Hg^0 trapped by the column, the reaction system was connected directly to the AA spectrometer.

3. Results and discussion

3.1. Preliminary results

Preliminary experiments were performed to determine the effectiveness of TiO_2 photocatalysis to remove methylmercury from aqueous solution. Since the reaction of Hg^{2+} reduction must occur at the conduction band electrons, the experiments were carried out in absence of oxygen avoiding the competition for electrons except when used for comparative purposes (as mentioned in the text). Fig. 1 shows the decay profile of mercury (II) in solution during the irradiation experiments under non-optimised conditions. Experiments in the dark indicate that the adsorption of CH_3Hg^+ on the catalyst surface is negligible at pH 7. Even at longer contact periods, no adsorption was evidenced. On the other hand, photolysis of methylmercury does occur, achieving maximum values after 30 min irradiation (35%). When irradiated in the presence of TiO_2 as catalyst, an evident Hg (II) removal, close to 100%, was observed after 10 min.

3.2. Optimisation of the reaction conditions

To identify the optimal values for the most important parameters associated to photocatalytic processes, an experimental design considering pH and the amount of TiO_2 was carried out. This procedure consists in the simultaneous change of the variables, identifying the conditions for the optimal degradation of $\text{CH}_3\text{Hg}^{2+}$ by performing a limited number of experiments. In a first step, optimisation was carried out in a wide domain of variables

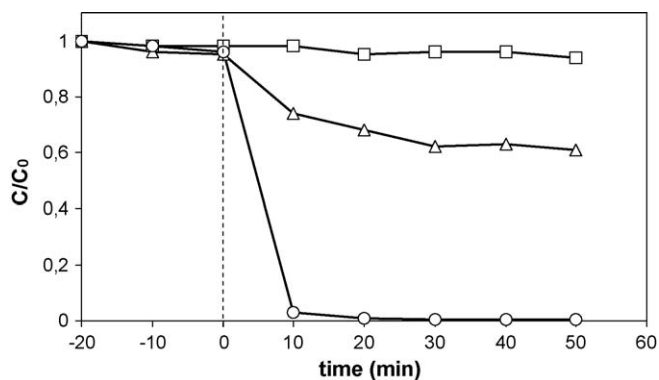


Fig. 1. Profile of mercury reduction by TiO_2 photocatalysis irradiated with visible light at pH 7 and under N_2 flow. (\square) Adsorption; (\triangle) photolysis; (\circ) TiO_2 photocatalysis (0.5 g TiO_2).

Table 1

Numerical results of the factorial experimental design of methylmercury removal assisted by TiO_2 and UV-A irradiation. The response factor was chosen as mercury reduction after 2 min irradiation.

Experiment	pH	TiO_2	%Hg removal	
			$Y_{\text{exp.}}$	$Y_{\text{calc.}}$
1	9 (−1)	0.06 (−1)	96.9	95.0
2	11 (1)	0.06 (−1)	98.0	98.6
3	9 (−1)	0.34 (1)	87.5	86.2
4	11 (1)	0.34 (1)	97.0	98.3
5	8.59 (− $\sqrt{2}$)	0.2 (0)	85.1	89.0
6	11.41 ($\sqrt{2}$)	0.2 (0)	99.9	100.0
7	10 (0)	0.002 (− $\sqrt{2}$)	97.0	97.7
8	10 (0)	0.40 ($\sqrt{2}$)	91.5	91.3
9	10 (0)	0.2 (0)	96.0	94.5
10	10 (0)	0.2 (0)	96.0	94.5
11	10 (0)	0.2 (0)	95.0	94.5

(pH: 4–10; TiO_2 : 0.2 – 0.8 g L^{-1}). Based in this preliminary approach, it was concluded that methylmercury degradation, measured as mercury reduction (Hg^{2+} to Hg^0), is enhanced at high pH and low amount of titania out of the chosen domain. In a second approach, a narrower domain was selected (pH from 9 to 11 and TiO_2 from 0.06 to 0.34 g L^{-1}), and the 11 experiments performed are shown in Table 1. The response factor was chosen as the percentage of mercury (II) reduced to Hg^0 after 2 min irradiation under nitrogen flow. In Table 1, real and codified values are shown. It is remarkable that several experiments indicate high degradation values ($>85\%$) in the presence of catalyst and UV-A irradiation. Using the response factor ($Y_{\text{exp.}}$), a polynomial that describes the reaction system was created (Eq. (8)). The validation of the mathematical model was performed by ANOVA test and is demonstrated comparing the experimental and predicted results ($Y_{\text{calc.}}$), calculated by using the polynomial. Values in parenthesis in the polynomial represent the standard deviation of each codified coefficient. Clearly, the most significant variable is the pH value. The reaction is favoured at high pH and low titania amount. No synergies or antagonism between the variables were found in the studied domain. Also no quadratic behaviour was shown.

$$Y = 94.5 (\pm 0.6) + 3.9 (\pm 0.7) \text{ pH} - 2.3 (\pm 0.7) \text{ TiO}_2 + 2.1 (\pm 1.0) \text{ pH} \cdot \text{TiO}_2 \quad (8)$$

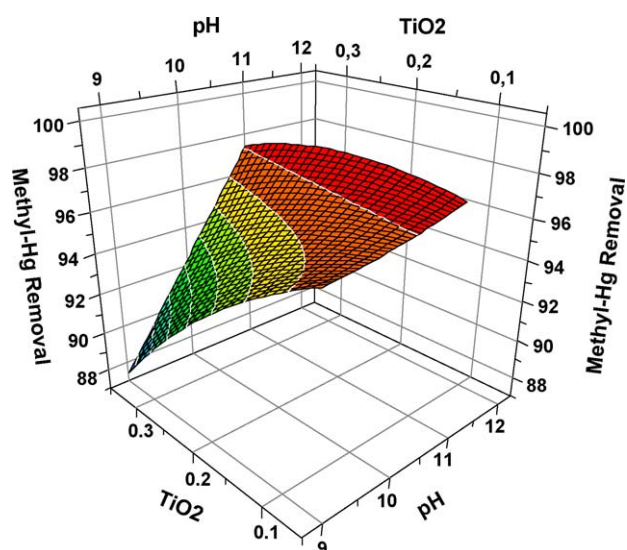


Fig. 2. Response surface of mercury reduction by TiO_2 photocatalysis as a function of pH and amount of catalyst. The reaction was conducted under nitrogen flow.

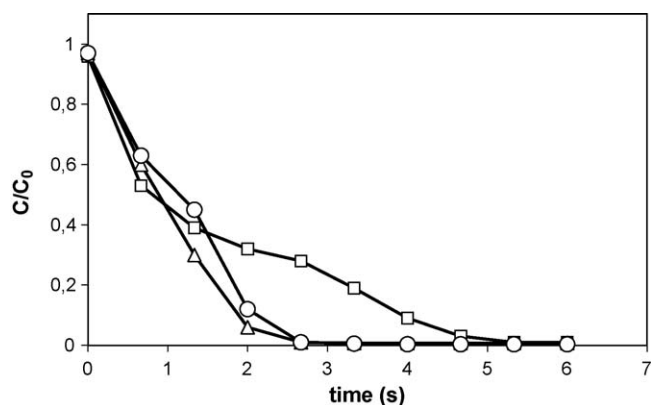


Fig. 3. Course of mercury reduction by TiO_2 photocatalytic system under different conditions. (Δ) Irradiation carried out by solarium device and nitrogen flow; (\square) irradiation with solarium device and oxygen flow; (\circ) irradiation by solar light and nitrogen flow.

A 3D representation of the polynomial is shown in Fig. 2, where it can be seen that the mercury (II) removal improves with increases in pH. In contrast, reaction performance is improved at low amount of catalyst, reaching the highest yield at around 0.15 g L^{-1} . No maximum pH value for MeHg removal was found. For practical purposes, the reaction's optimised conditions were selected as pH 11 and 0.15 g L^{-1} of catalyst. Further experiments were carried out under such conditions. The fact that the reaction yield is improved at high pH could be related to the catalyst's negative surface charge at this pH ($\text{ZPC} \sim 6.1$), inducing a high adsorption of the CH_3Hg^+ cation. It is important to mention that methylmercury chloride is a weakly dissociated species, and thus the adsorption phenomenon is not as significant as expected. On the other hand, the low amount of catalyst is consistent with the substrate's low concentration. Indeed, it allows higher quantum yields due to the decrease in light scattering. Under optimised conditions, the complete reduction of Hg^{2+} by photocatalysis occurs after 3 min irradiation in the presence of nitrogen (Fig. 3). In the presence of oxygen, the reduction profile changes, decreasing the reaction's effectiveness. In the last case, the reaction reaches the same reduction yield after around 5 min. These results can be explained as due to the competition between Hg^{2+} and O_2 for the conduction band's electrons.

In order to evaluate the effectiveness of the solar light-driven process to remove methylmercury from aqueous solutions, an experiment was performed with direct irradiation by sun light (December 2007, latitude 36.7° south, 1.92 mW cm^{-2} measured at 360 nm). The reaction profile (Fig. 3) is comparable to the one obtained under artificial light, indicating the potentiality of use this technology to treat liquids or soils contaminated with methylmercury.

3.3. Quantification of Hg^0 in the gas phase

In experiments done coupling the reactor to the atomic absorption spectrophotometer, the on-line detection of Hg^0 was possible. Fig. 4 presents the mercury evolution from the methylmercury solution ($100 \mu\text{g L}^{-1}$, Hg basis) under nitrogen flow (100 mL min^{-1}) in comparison with a Hg^{2+} standard solution at the same concentration. The standard solution of Hg^{2+} was completely reduced by SnCl_2 addition (Fig. 4a). Conversely, the signal depicted in Fig. 4b confirms that Hg^0 is formed after few minutes irradiation in the presence of TiO_2 . Mercury was quantified as a cold vapour in the AAS device. Considering that the area under the standard's curve represents 100% of the Hg^0 released, the amount of mercury reduced by photocatalysis correspond to around

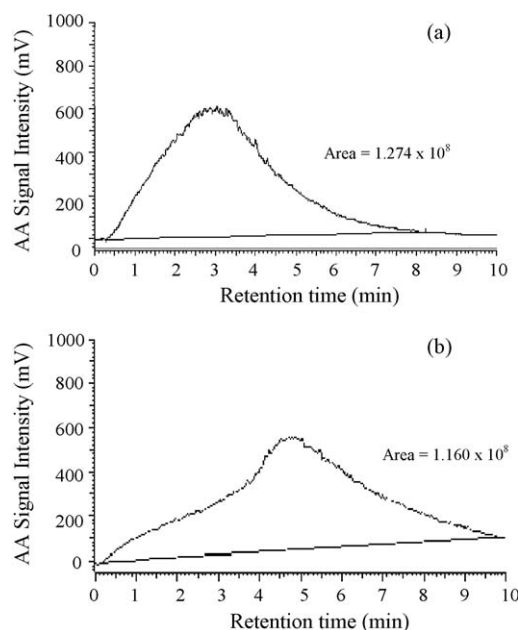


Fig. 4. Hg^0 evolution from methylmercury solution under N_2 stream. Signals were obtained by AA spectrometer. (a) Hg^{2+} standard solution reduced with SnCl_2 ; (b) photocatalytic reduction of methylmercury at pH 11 in the presence of TiO_2 (0.15 g L^{-1}).

91%. It is important to point out that the delay observed in the Hg^0 evolution (Fig. 4b), when compared to the short time required to remove all the Hg^{2+} from the aqueous solution (Fig. 3), can be explained by the high dead volume in the reactor (250 mL).

3.4. Effect of the initial methylmercury concentration

The effect of the initial MeHg concentration was determined under optimised conditions using the solarium device under nitrogen flow. Considering that the degradation of most of the organic compounds is well described by a pseudo-first-order kinetic for dilutes solutions, the Langmuir–Hinshelwood (L–H) mechanism can be adjusted for the studied system. Even when there is no consensus with respect to the use and interpretation of the L–H model, its use is recommended due to its simplicity and accurate adjustment to experimental values [18]. In order to confirm the heterogeneous catalytic character of the reaction, the initial rate (r_0) was determined at different concentrations (C_0), ranging from 50 to $250 \mu\text{g L}^{-1}$. By using the linearized L–H model ($1/r_0 = 1/k_0 + 1/k_0 K C_0$), both constants K and k_0 were graphically calculated. K represents the equilibrium constant for monolayer substrate adsorption on TiO_2 surface and k_0 the reaction's limiting rate at maximum coverage for experimental conditions. Calculated values were $k_0 = 1.359 \times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$ and $K = 2.881 \times 10^5 \text{ L mol}^{-1}$. Adjustment of the L–H model to the studied reaction system indicates that adsorption is the critical step of the reaction. Our results agree well with the increase in the reaction rate at alkaline pH, when the maximum adsorption is reached due to the attraction between the positive CH_3Hg^+ and the catalyst's induced negative surface.

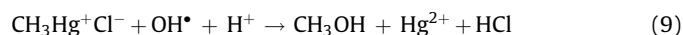
3.5. Figure-of-merit: electric energy per order

The figure-of-merit electric energy per order of magnitude (E_{EO}) provides a direct link to the electric- or solar-energy efficiency of an advanced oxidation technology (AOT) [19]. It can be applied for low contaminant concentrations and has been used to compare different AOTs. In the case of methylmercury degradation, the calculated E_{EO}

value was $39 \text{ kWh m}^{-3} \text{ order}^{-1}$. This figure was calculated from the semi-logarithmic plot $100 C/C_0$ vs. UV dose (kWh m^{-3}) considering that the irradiation was carried out in a solarium device (120 W). Depending on the structure of the contaminant and the AOP used, reported values are rather variable. For instance, they can range from around 10 to over $140 \text{ kWh m}^{-3} \text{ order}^{-1}$ [15,20]. To the best of our knowledge, no data are available for organometallic compounds, such as methylmercury.

3.6. Identification of gaseous degradation products

The gases released from the reaction system operated at optimised conditions were analysed connecting the photochemical reactor to a GC equipped with a thermal conductivity detector. The profile of released gases were compared to a Fisher–Tropsh gas mixture, which consists of CO , H_2 , CO_2 , CH_4 and N_2 in a well-established ratio. Experiments carried out under nitrogen stream reveal that no gases are released in the course of the reaction. This result can be explained by the formation of water soluble non-volatile compounds, such as methanol, and their oxidation by-products in a mechanism shown in Eq. (9). Methanol was detected in the solution after 2 min of irradiation by GC/MS analysis. Methanol can be further directly oxidised by holes (h^+) formed in the valence band (Eq. (10)). This mechanism has been recently proposed for the phenylmercury degradation by TiO_2 [9]. On the other hand, Hg^{2+} is reduced to zero valent mercury by conduction band electrons in a sequential process Eq. (11).



On the other hand the evolution of CO , CO_2 and CH_4 in the course of the reaction performed under oxygen bubbling was observed. Using the F–T mixture as standard, the gases released from the reaction system were quantified. The methyl group was found to be completely converted into CH_4 , CO and CO_2 . The initial amount of carbon in the sample was 0.6 mg (based on 107 mg L^{-1} of CH_3Hg^+); After the reaction, 0.11 mg of C as methane, 0.33 mg of C as CO and 0.19 mg of C as CO_2 were recovered. Those amounts correspond to 17.5, 52.5 and 30% respectively of the total carbon. The total recovery of carbon was around 105%, where the excess calculated can be attributed to experimental error. It is important to mention that the methyl group is the only carbon source present in the initial solution. These results indicate that most of the reaction occurs via the oxidative pathway, under oxygen bubbling. The formation of CO and CO_2 can be explained by the multiple manners that oxidation can occur under oxidative conditions. Among others, the oxidation of methyl group (or methane, or methanol) can occur directly by holes or by the attack of radicals formed in the presence of oxygen (OH^\bullet , OOH^\bullet , $\text{O}_2^{\bullet-}$). On the other hand, methane can be formed by splitting the methyl group and mercury followed by hydrogen abstraction.

3.7. Trapping of Hg^0 vapour by copper pellets

In general, heavy metals such as Hg^{2+} have been removed by direct deposition on metal reducers such as Al , Fe , Cu or Zn , among others [3,21]. Nevertheless, those reducers are released to the solution creating a new pollution source. In order to avoid this drawback, Cu^0 was used in this study to form an amalgam with the released Hg^0 vapour. Due to the high toxicity of Hg^0 , the emission of this vapour into the atmosphere could be considered as a disadvantage of the photocatalytic process. In order to avoid this

potential drawback, a trap with copper powder was used to immobilise Hg^0 in the form of Cu – Hg amalgam as was previously suggested for mercury reduced in aqueous solutions [21]. Three copper forms were assayed: chips, thin foils ($0.5 \text{ cm} \times 0.5 \text{ cm}$) and fine powder ($<63 \mu\text{m}$). The best retention yields were obtained by using copper powder resulting in a high amalgamation yield with a recovery above 90% as determined by AAS. Those results suggest that the photocatalysis of methylmercury followed by Hg^0 amalgamation with metallic copper could be promissory in the treatment of methylmercury-contaminated solutions or other organometallic compound.

3.8. Conclusions

Based on our experimental results, we summarize the most remarkable conclusions:

1. TiO_2 –heterogeneous photocatalysis is able to reduce Hg^{2+} to Hg^0 from methylmercury solutions in a very efficient and fast conversion concomitant with the destruction of the organic matter.
2. The reaction proceed in a better way at alkaline conditions (pH 11) and with a low catalyst amount (0.15 g L^{-1}).
3. Methylmercury can be removed in the presence of nitrogen or oxygen following different mechanism pathways.
4. In the presence of nitrogen the reaction proceeds by forming water soluble compounds such as methanol.
5. In saturated oxygen solutions, the formation of CO and CO_2 and a minor amount of CH_4 suggests a mechanism where the methyl group was mostly oxidised.
6. Hg^0 vapours can be easily retained by copper powder forming an amalgam.
7. The energy cost to remove CH_3Hg^+ in one order of magnitude of 90% turns out to be $39 \text{ kWh m}^{-3} \text{ order}^{-1}$.
8. Considering the reaction's high efficiency under solar light, this process can be applied at low cost.

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